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Synthesis of Poly Vinyl Pyrollidone Capped SrO_2. Hydrate Nano Flowers by Novel Micro Flow Reactor and the Size Characterizations

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ABSTRACT

Strontium peroxide is one of the most useful alkaline oxides which find variety of applications. Though there are few conventional methods of preparing Strontium Peroxide (SrO_2) available in the recent literature, we have developed a Special Continuous Co precipitation technique carried out in Novel Micro Flow Reactor. This method attracts our attention for the novelty of its design. This method is so precise in isolation of Nano Flowers of Strontium peroxide of high purity and homogenous nano crystallites with monodispersity. The size, shape can be controlled by the factors such like concentrations of precursor solution ($SrCl_2.6H_2O$), Co precipitant-NaOH, Surfactant-Sodium Dodecyl Sulphate(SDS), Capping agent Poly Vinyl Pyrrolidone(PVP) concentration. The size and shapes of the Nano Flowers of SrO_2 is characterized by XRD, SEM methods.

Keywords: Nano flowers of SrO_2 Hydrate, Micro Flow Reactor, Co precipitation technique, PVP capped SrO_2.

1. INTRODUCTION

Strontium Oxide SrO and Strontium peroxide SrO_2 are well known industrially important compounds and components in clay, special glass and ceramic products[1]. Strontium develops vivid colors that can improve the surface of high viscous

zirconium fireproof ceramics and glazes[2]. It is because of its non- hazardous, non-poisonous nature and viable substitute to BaO and PbO. SrO_2 is used as starting component in making oxide-coated cathodes for electric vacuum devices[3]. In manufacturing of glasses for color TV+ displays and monitors as a protection from X-rays[4]. It is used to prepare ferro strontium powders used to make ceramic hard ferrites[5].

SrO_2 as a feedstock to manufacture other strontium compounds, such as strontium chromate, strontium chloride, metal strontium and others. The picture tube glass in television contains about eight percent of strontium oxide[6]. It has an expansion akin to CaO and a similar decomposition behavior. The heat of Sr-90 radio isotope can be converted to electricity for long-lived, lightweight power sources in navigation buoys, remote weather stations, space vehicles[7] etc., SrO_2 grains are used in various pyrotechnic devices, flares, and tracer bullets[8-15]. Strontium hydroxide, $Sr(OH)_2$, is also used to extract sugar from molasses because it
forms a soluble saccharide from which the sugar can be easily regenerated by the action of carbon dioxide. Strontium monosulfide, SrS is employed as a depilatory and in some luminous paints. But due to the costlier nature, it is not widely used as CaO and BaO which are the relatively abundant and cheaper counter parts.

SrO_2 crystals occur in tetragonal structure with BCC lattice units. Nano crystallites of SrO_2 can be prepared by Co precipitation followed by calcinations, Flame pyrolysis of carbonate salts, Sol-gel, Hydrothermal, Microwave–plasma, Double decomposition etc.,

In our present work, we have developed a simple continuous co precipitation method of preparing Nano flowers of SrO_2 through Micro Flow reactor. It is easy to operate, less time consuming, involves lesser expensive instrumentation and lesser power consuming method of operation. It is also proved to be a standardized method for making nano crystallites with fair monodispersity. This method can also be extended for large scale preparation on nano flowers of SrO_2 by using large scale batch reactors involving proportionate dimensions.

2. MATERIALS & METHODOLOGY

2.1 Preparation of Strontium peroxide Hydrate Nanoparticles:

This wet chemical method involves co precipitation of Strontium Hydroxide from precursor and alkali solutions followed by thermal treatment of the hydroxide residue thus yielding PVP capped nano flowers of SrO_2. Polyvinyl Pyrrolidone (PVP) solution acts stabilizer cum capping agent. In the I-batch, 50 ml of 0.1M solution of $SrCl_2.6H_2O$ (Precursor-1) is loaded with 1 ml of 0.1wt % PVP solution and 1ml of 0.1wt %SDS solution taken in a vertical burette like cylinder.50 ml of 1M NaOH(Co precipitant) is taken in another vertical burette like dispenser. The nozzles of both dispensers are fitted with a special micro dispensing valve. The precursor and the Co precipitant solutions are added simultaneously by micro flow stream of droplets using a special micro syringe valve into the 200ml three necked round bottomed flask on a magnetic stirrer at 45^0C temperature. The addition results in the

formation of gelatinous cloudy white $Sr(OH)_2$ precipitate.

The suspension is ultra centrifuged at 3000 rpm for 30 minutes. The spongy hydroxide residue is washed three times with deionised water and filtered in whatman 1 filter paper. The residue is calcined in vacuum oven at 120^0C for 24 hours yielding spongy nano flowers of SrO_2 with homogeneity.

The effect of dilution is studied by taking 0.05M $SrCl_2.6H_2O$ solution, 0.02 wt %of PVP solution and 0.5M NaOH solution and repeating the procedure as in Batch-1 exactly. This run is taken as Batch-2. The dispensing nozzles have different orifice diameters. Micro tips (Eppendorf type) commonly used in Biostep Micropipettors with fixed volumes, one channel volume with 25 µl /50 µl / 100 µl per droplet can be used for our micro flow reactor, by attaching such micro tips to burette's(additional cylinders)dispensing nozzle.

This can be achieved by adjusting for 40 drops per ml or 20 drops per ml flow rate and can be constantly maintained. The rate of addition can also be controlled to 1 ml for twenty seconds (50µl per sec).

The reaction is carried out for 17 minutes for the I Batch. The rate of addition can also be controlled to ml for forty seconds (25µl per sec).The reaction is carried out for 34 minutes for Batch-2. A three necked round bottomed flask is set up as in the diagram over the magnetic stirrer. The condenser shown in the diagram is for water inlet and outlet for cooing purpose as the reaction is exothermic. Nitrogen atmosphere is provided by a balloon to the round bottomed flask reflux condenser.

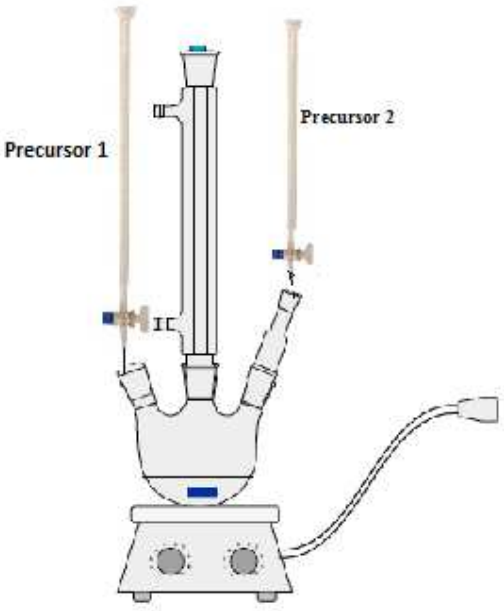

Fig.1 Micro flow reactor assembly technique for the preparation of Nano Flowers of SrO_2 $8H_2O$ by coprecipitation.

Table-1 Details of the Batches Conducted

BATCH	Precursor-1	(Co precipitant) Precursor--2	Size of $SrO_2.8H_2O$ NP ±1 nm
Batch-1	0.1M $SrCl_2.6H_2O$ solution + 1ml of 0.1% PVP Solution + 1ml 0.1% SDS solution	1 M NaOH solution	119.82
Batch-2	0.05M $SrCl_2.6H_2O$ solution + 2ml of 0.2% PVP solution+1 ml 0.1% SDS soln.	0.5M NaOH solution	29.89

3. RESULTS AND DISCUSSION

The powder X-ray diffraction studies on the synthesized nanoparticles were performed using Rigaku diffractrometer (Model: Ultima III, Japan) using CuK_{α} (1.54 A°) radiation.

A beam voltage of 40 kV and a beam current 30 mA were used. The data were collected in the 2θ range (10 - 80°) with a continuous scan speed of 0.2 deg./ min.

The size of the particles has been computed from the width of first peak using Debye Scherrer formula, $D = K\lambda/\beta \cos\theta$,

Here K is is a constant usually taken to be unity, λ is the wavelength of X-rays employed radiation (1.54056 Å), β is corrected full width at half maximum and θ is Bragg angle. The average crystallite size (D_v) from X-ray line broadening of prominent diffracted peak, β_{hkl} is the full width at half maximum (FWHM) located at 2θ and θ is the angle of reflection(in degrees).To eliminate the additional instrument broadening, FWHM was corrected using the FWHM from a large grained Si sample.

It is evident that for dilute concentrations of precursor-1 and precursor-2 with load of excess capping agent of higher concentration results in the formation of smaller particles due to the micro emulsion formation.

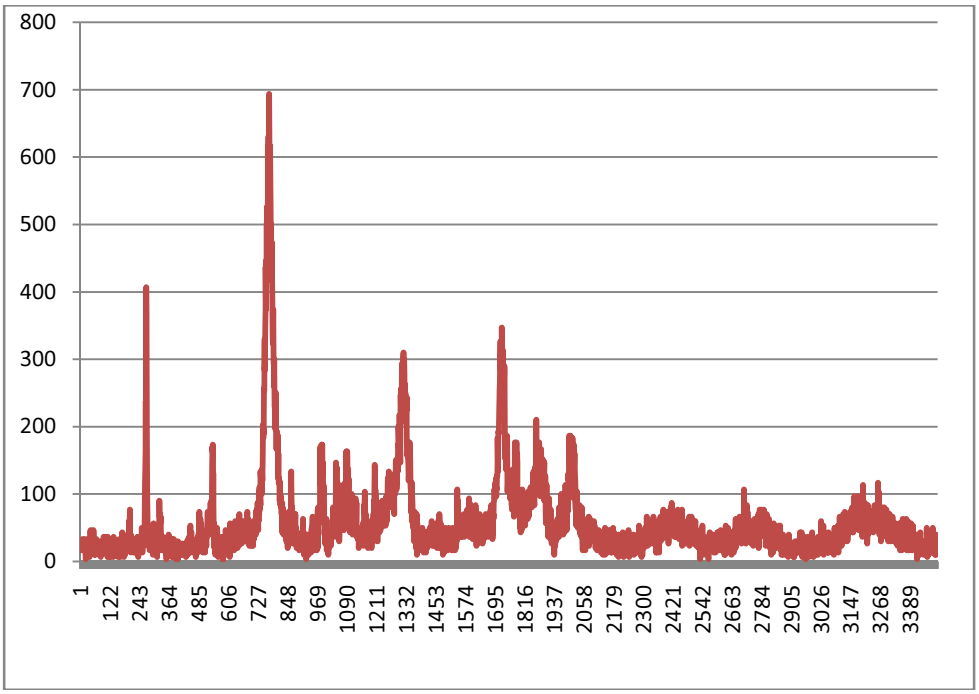

Fig.2 X-Ray powder diffraction pattern of PVP protected $SrO_2.8H_2O$ nanoparticles of Batch-2 sample.

The above X-ray powder diffraction (XRD) pattern confirms the hydrated nano particles of $SrO_2.8H_2O$ which compared and agree well with the pattern of card number (JCPDS FILE NO: 75-1137) of international XRD data base with ICSD # 030573.The very broad XRD peak around $2\theta = 25.12^0$ is assigned to amorphous PVP. The other peaks at 2θ = 15.40, 20.80, 25.34, 25.76 and 44.42 correspond to 100,110 112, 200, and 222 planes of the Tetragonal cubic space group.

FTIR spectra are obtained for the nanoparticles to show the presence of PVP moiety. The band at 1658 cm−1 is assigned to the stretching vibration of the C=O in the PVP amide unit. The other peaks such as band at 1285cm^{-1} and 1425 cm^{-1} are all the typical adsorption bands of PVP. Both the XRD and FTIR results confirm the formation of PVP-protected Hydrated SrO_2 nanoparticles by the co precipitation method.

Table-2 XRD data for the Strontium peroxide Hydrate ($SrO_2.8.H_2O$) of Batches 1 and 2

Batch	2θ value from XRD graph	D Value for I/I_0 =100	Intensity maximum for FWHM β value	Size of NP ±1 nm
Batch-1	25.34	3.5119	0.071	119.82
Batch-2	24.92	3.4995	0.285	29.89

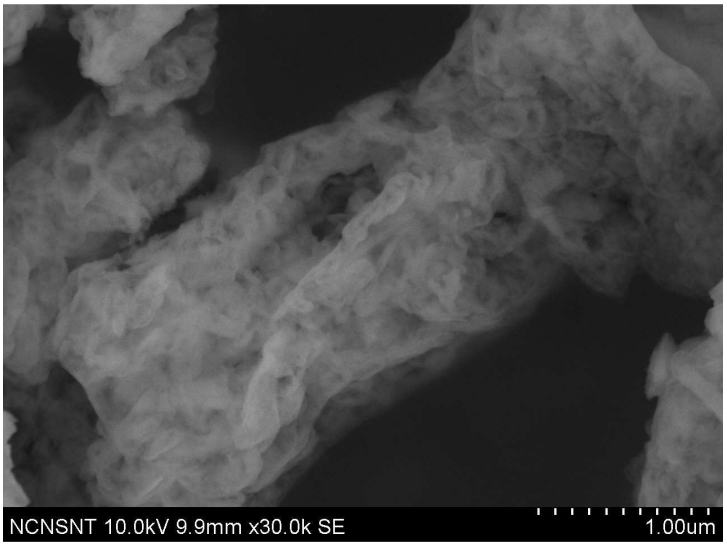

Fig.3 SEM Image of PVP capped Nano flowers of $SrO_2.8H_2O$

The SEM analysis is done at NCNST facility of University of Madras. The surface morphology of the nanocrystallites were analyzed with the help of JEOL JSM-6360 Scanning Electron Micrograph instrumentation facility. SEM images of the sample clearly indicates the encapsulated SrO2.Hydrate nanoparticles by PVP matrix in a lower resolution shown in Fig-3.The higher resolution version of

SEM image depicted in Fig-4 which clearly shows the $SrO_2.8H_2O$ nanoflowers in which the petals are oriented upwards with a breadth of around 20-30 nm.

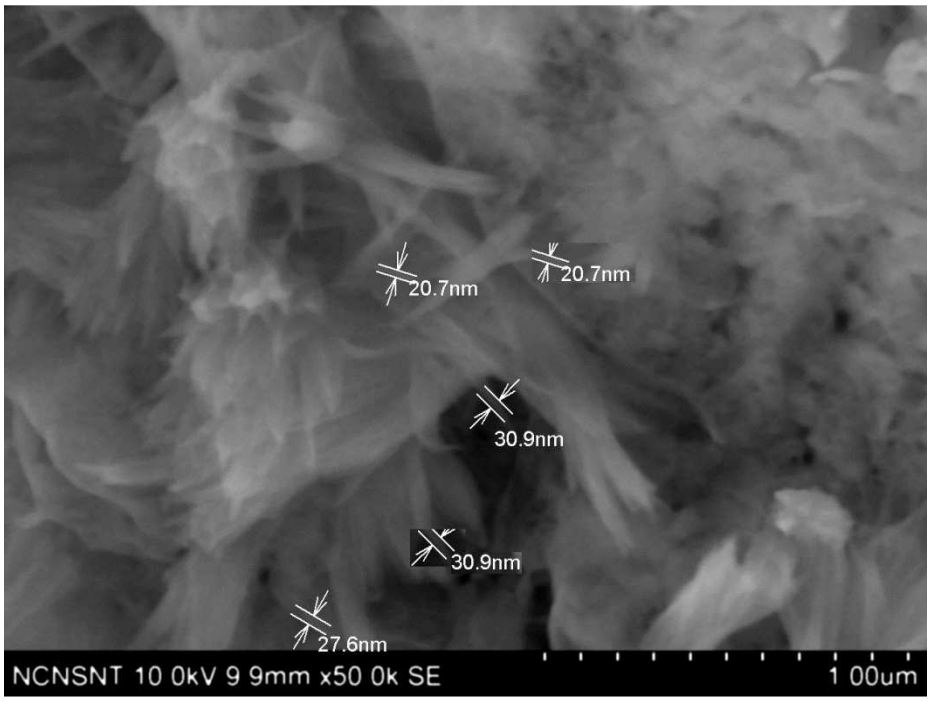

Fig.4SEM image of Nano flowers of $SrO_2.8H_2O$

Estimation of average crystallite size of synthesized nanomaterials

X-ray line broadening analysis provides a method of finding an average size of coherently diffracting domains. The average crystallite size (D_v) from X-ray line broadening of prominent diffracted peak, could be calculated using Debye-Scherer formula, $D_v = \frac{k\lambda}{\beta_{hkl}\cos\theta}$ where, D_v is the average crystallite size, k is a constant usually taken to be unity, λ is the wavelength of CuK_α radiation, β_{hkl} is the full width at half maximum (FWHM) located at 2θ and θ is the angle of reflection (in degrees).To eliminate the additional instrument broadening, FWHM was corrected using the FWHM from a large grained Si sample.

The powder X-ray diffraction studies on the synthesized nanoparticles were performed using Rigaku diffractrometer (Fig. 2.1(b)) (Model: Ultima III, Japan) using CuK_α (1.54 A°) radiation. A beam voltage of 40 kV and a beam current 30 mA were used. The data were collected in the 2θ range (10 - 80°) with a continuous scan speed of 0.2 deg./min.

X-ray Powder Diffraction (XRD) at NIT Tiruchi

XRD unit

4. CONCLUSION

The above results indicate the influence of quantity of surfactants and capping agent as deciding factors for size of SrO_2Hydrate particles. This is due to decrease in water to surfactant ratio in the reaction mixture. The water-to-surfactant molar ratio is increased in the second case enhancing micro emulsion formation due to the contact time of one day after the addition of PVP the reactions were carried out. This

resulted in the formation of smaller nano crystallites in the second batch of co precipitation involving dilute precursor concentrations.

Our method utilize simple economic instrumentation for achieving nanoparticles of desired size by controlling the concentration of the precursors, co precipitant, choice of surfactants, concentration of capping agent, size volume of the droplet (micro orifice size of dispensing nozzle) and flow rate of the two mixing solutions, reaction temperature. The surface tension and viscosity of all the mixing solutions along with chosen surfactants are carefully standardized after many trials.

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